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THE MELTING POINT AND THE HEAT OF SUBLIMATION OF PuF_3

Edgar F. Westrum, Jr. and James C. Wallmann

May 19, 1950

Berkeley, California

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THE MELTING POINT AND THE HEAT OF SUBLIMATION OF PuF_3*

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May 19, 1950

Careful measurements by an effusion technique of the equilibrium vapor pressures over plutonium trifluoride have been reported.(1) The slight deviation from

(1) T. E. Phipps, G. W. Sears, R. L. Seifert, and O. C. Simpson, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 6.1a (McGraw-Hill Book Co., Inc., New York, 1949).

linearity of the log p versus 1/T plot was represented by these authors without a stated reason as two straight lines intersecting at 1169 ± 9°C., which temperature was interpreted as the melting point of PuF_3. The heat of fusion was reported as 7.9 ± 0.5 kcal./mole with a heat of sublimation of 96.6 ± 0.5 kcal./mole. Inasmuch as the deviation from linearity may alternatively be accounted for by assuming a reasonable ΔCp for the sublimation process and as the reported melting points are rather lower than would be expected from comparison with other fluorides,(2)

(2) L. Brewer, L. Bromley, P. W. Gilles, and N. L. Lofgren, ibid., Paper No. 6.40.

we have undertaken a determination of the PuF_3 melting point in the apparatus shown in Fig. 1. An inconclusive attempt to determine the PuF_3 melting point using about 60 micrograms of material on a degassed tantalum filament in purified argon yielding successive values of 1435, 1560, and 1635°C. has been reported.(3)

(3) H. P. Robinson, Manhattan Project Metallurgical Laboratory Report CN-2159 (Oct., 1944).

*Based on work reported in MB-IP 327, September 17, 1948.

X-ray diffraction examination indicated the formation of PuOF in the sample. For the present work about 250 mg. of PuF_3 were prepared by hydrofluorination in a platinum reactor[4] of uranium-free, spectroscopically pure plutonium dioxide.

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(4) E. F. Westrum, Jr., "The Preparation and Some Properties of Americium Metal," in preparation.

X-ray diffraction examination and spectrochemical analyses after the measurements confirmed the purity and phase of the PuF_3 and the absence of corrosion of the tantalum.

Continuous potential curves of the platinum versus platinum plus 10% rhodium thermocouple were automatically traced on a Leeds and Northrup Speedomax recorder checked against a Rubicon Type B potentiometer. These curves were essentially interpolations over ten to thirty degree ranges, the limits of which were established by direct optical pyrometer observation of the tantalum crucible at temperature equilibrium. Since essentially "black body" conditions obtain for the tantalum crucible, no emissivity correction is involved. Both optical pyrometers were calibrated against a standard lamp and also against the melting point of palladium in the present apparatus upon substitution of a beryllia liner. Direct observation of the fusion and solidification points with the optical pyrometer were found to agree with the thermocouple values and with each other regardless of the sign or magnitude of the thermal head. Corrections were applied for the transmissivity of the pyrex window and after many transitions a compensation amounting to several degrees was required to correct for the sublimed film of plutonium trifluoride on the window. Repeated transitions were observed under various thermal heads both in high vacuum and under 10^{-2} atm. of argon as follows:

Fusion temperature (11 observations): $1426 \pm 2^{\circ}C$.

Solidification temperature (13 observations): $1425 \pm 3^{\circ}C$.

The uncertainties indicated are average deviations. No thermal effect was detected near the temperature previously interpreted as the melting point.[1]

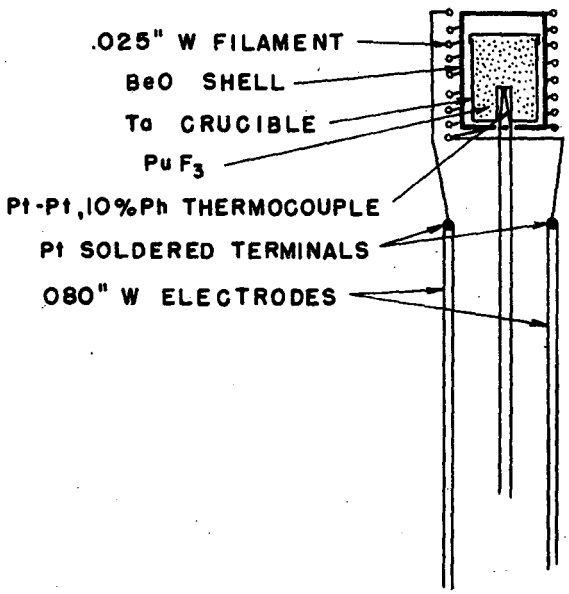
Using the Gaussian criterion for closeness of fit, a three constant equation fitted by weighted least squares indicated as good agreement with the vapor pressure data as did the two similarly fitted linear equations previously reported.

The ΔCp of sublimation corresponding to this equation was -32 cal. $mole^{-1}$ $deg.^{-1}$. A least squares treatment with an assumed value of $\Delta Cp = -15$ cal. $mole^{-1}$ $deg.^{-1}$ and two arbitrary constants also fits the data well and yielded the equation

$$\log_{10} P_{mm} = -24{,}917\ T^{-1} - 7.5513 \log T + 38.920$$

valid from 1200 to 1660°K. for the dissociation pressure and a value of 89 kcal. $mole^{-1}$ for the heat of sublimation at 1400°C.

The experimental work was performed under the auspices of the U. S. Atomic Energy Commission at the University of California Radiation Laboratory.



PuF_3 MELTING POINT APPARATUS

MU 324

FIG. 1